FURTHER PROGRESS IN FITTING 13000 TORSION-WAGGING-ROTATIONAL MW AND IR v_t = 0,1 TRANSITIONS IN CH_3NH_2 USING THE HYBRID (TUNNELLING + INTERNAL ROTATION) PROGRAM

ISABELLE KLEINER, *Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS et Universités Paris Est et Paris Diderot, Créteil, France*; JON T. HOUGEN, *Sensor Science Division, National Institute of Standards and Technology, Gaithersburg, MD, USA*.

A few years ago, the authors wrote a hybrid program to fit rotational levels in molecules with one CH_3 internal-rotation large-amplitude motion, one NH_2 inversion large-amplitude motion, and symmetry described by the G_{12} PI group. This program was applied with success to the MW spectrum of 2-methylmalonaldehyde, but the rather small data set for this molecule did not provide a stringent test of the model. More challenging is the application of the hybrid program to CH_3NH_2, since this molecule has a much larger data set, containing both MW and IR transitions, as well as having a more extensive v_t, J, and K quantum number coverage. In our ISMS talk this year we will first give an overview of our best least-squares fit to date: The data set contains slightly more than 2500 MW and 11000 IR transitions with $J \leq 32$ and $K \leq 14$, which are fit to a weighted standard deviation of 1.64 using 71 parameters. Next, we present an assessment of this fit's strong points (e.g., significantly less parameters, ability to predict spectra in higher torsional states) and weak points (e.g., somewhat larger standard deviation, greater parameter correlation) when compared to the best all-tunneling-model fit in the literature. Based on this assessment, we believe that our fit, as well as the predictive abilities of the program, are sufficiently good that we can now begin considering collaborations with measurement and assignment campaigns of v_t = 1 MW data and v_t = 2, 3 IR data already underway in other laboratories. Finally, we will present a slightly modified ordering scheme for the operators in this hybrid program, and describe the need for devising a contact transformation treatment to specify determinable parameters in the hybrid Hamiltonian, in order to reduce parameter-correlation problems during the trial-and-error fitting process. A knowledge of determinable parameters would be particularly useful here, since there is little previous experience to guide the choice of "a good set" of higher-order constants to float when carrying out large fits having over 10000 lines, J_{max} = 40, K_{max} = 15, v_t = 0 and 1 torsional states, A_1, A_2, B_1, B_2, E_1, E_2 symmetry species, and nearly 100 parameters.